ON THE POSSIBLE FORM OF THE EQUATION OF STATE OF POWDER GASES

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It has been customary for ballisticians to make use of the equation proposed by Clausius,

$$\left\{p + \frac{a}{T(v+\beta)^2}\right\}(v-\alpha) = RT, \tag{1}$$

in the simplified form, suitable for the high temperatures concerned,

$$p\ (v - \alpha) = RT. \tag{2}$$

At the same time it is customary to make use of the experimental results of Mallard and le Chatelier and of Berthelot and Vieille on the specific heats which state that C_v is a linear increasing function of the temperature. While apparently no experiments have been made on C_p it is assumed that the difference of the specific heats is constant, as in the case of an ideal gas.

It has occurred to me to examine the question of the most general form possible for the equation of state that shall permit of variability of the specific heats, but maintain the constancy of their difference. This question does not appear to have been treated,

By an application of the two laws of thermodynamics we obtain the well-known equation

$$(C_p - C_v)\frac{\partial T}{\partial p}\frac{\partial T}{\partial v} = T. \tag{3}$$

If we use the usual letters for differential equations, putting x for v, y for p, z for T divided by $C_p - C_v$ supposed constant, and as usual p for $\partial z/\partial x$, q for $\partial z/\partial y$ we have the very simple partial differential equation,

$$F = p\,q - z = 0. \tag{4}$$

This may be very simply integrated by Cauchy's method, which consists in integrating the system

$$\frac{dx}{P} = \frac{dy}{Q} = \frac{dz}{Pp + Qq} = -\frac{dp}{X + pZ} = -\frac{dq}{Y + qZ} = \frac{du}{q},$$

where the capital letters represent the derivatives of F with respect to the corresponding small letters, and u is an extraneous parameter. Having found

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five integrals, with five arbitrary constants x_0, y_0, z_0, p_0, q_0 we make the latter functions of a second parameter v satisfying the equations

$$p_0 q_0 - z_0 = 0, \quad \frac{\partial z_0}{\partial v} = p_0 \frac{\partial x_0}{\partial v} + q_0 \frac{\partial y_0}{\partial v}. \tag{5}$$

We easily obtain the five integrals,

$$x - x_0 = u, \quad y - y_0 = \frac{p_0}{q_0} u, \quad \frac{p}{p_0} = \frac{q}{q_0}, \quad q - q_0 = u,$$

$$z - z_0 = 2 p_0 u + \frac{p_0}{q_0} u^2, \text{ with } p_0 = \frac{z_0}{q_0}.$$

Instead of adopting Cauchy's form for the introduction of the arbitrary function, we will attempt to pass the integral surface through the plane $z_0 =$ *const.*, representing an isothermal. We put

$$\begin{aligned} &x_0 = v, \quad y_0 = \varphi(v), \quad p_0 + q_0 \varphi'(v) = 0, \quad \frac{z_0}{q_0^2} = -\varphi'(v), \\ &y = \varphi(v) - u\varphi'(v), \\ &z = z_0 \pm 2\sqrt{-z_0\varphi'(v)}\, u - \varphi'(v)u^2, \\ &x = u + v. \end{aligned} \tag{6}$$

If we adopt the Clausius equation for the form of one particular isothermal, we may put

$$\begin{aligned} \varphi(v) &= \frac{Rz_0}{v - \alpha} - \frac{a}{z_0(v+\beta)^2}, \\ \varphi'(v) &= -\frac{Rz_0}{(v-\alpha)^2} + \frac{2a}{z_0(v+\beta)^3}. \end{aligned} \tag{7}$$

We thus obtain finally

$$\begin{aligned} &x = u + v, \\ &y = \frac{Rz_0}{v-\alpha} - \frac{a}{z_0(v+\beta)^2} + u\left\{\frac{Rz_0}{(v-\alpha)^2} - \frac{2a}{2_0(v+\beta)^3}\right\} \\ &z = z_0 \pm 2u\sqrt{z_0\left(\frac{Rz_0}{(v-\alpha)^2} - \frac{2a}{z_0(v+\beta)^2}\right)} + u^2\left\{\frac{Rz_0}{(v-\alpha)^2} - \frac{2a}{z_0(v+\beta)^3}\right\} \end{aligned} \tag{8}$$

so that we have the parametric equation of the surface. It may be noted that putting $u = 0$, $z_0 = T$ we fall back on the ordinary Clausius equation (1) as a particular case, with (2) and the ideal gas equations as still more particular.

In order to obtain the expression for the energy for such a gas, we make use of the equation

$$U = \int \left[\left(T \frac{\partial p}{\partial T} - p \right) dv + C_v dT \right], \tag{9}$$

in which we have now to put

$$\frac{\partial p}{\partial T} = \frac{\partial(p, v)}{\partial(x, y)} \Big/ \frac{\partial(T, v)}{\partial(x, y)}$$

We have now to make use of equations (6) in which, replacing the usual thermal notation, and now using x and y for the arbitrary parameters,

$$\begin{aligned} T &= T_0 \pm 2x\sqrt{-T_0\varphi'(y)} - x^2\varphi'(y), \\ p &= \varphi(y) - x\varphi'(y), \\ v &= x + y, \end{aligned} \tag{10}$$

$$\frac{\partial p}{\partial x} = -\varphi'(y), \quad \frac{\partial p}{\partial y} = \varphi'(y) - x\varphi''(y), \quad \frac{\partial v}{\partial x} = \frac{\partial v}{\partial y} = 1,$$

$$\frac{\partial T}{\partial x} = \pm 2\sqrt{-T_0\varphi'(y)} - 2x\varphi'(y),$$

$$\frac{\partial T}{\partial y} = \varphi''(y)\sqrt{-\frac{T_0}{\varphi'(y)}} - x^2\varphi''(y),$$

so that finally

$$U = \int \Bigg[\left(T_0 \pm 2x\sqrt{-T_0\varphi'(y)} - x^2\varphi'(y) \right) \left\{ \frac{-2\varphi('y) + x\varphi''(y)}{2\sqrt{-T_0\varphi'(y)} - 2x\varphi'(y) - \varphi''(y)\sqrt{-\dfrac{T_0}{\varphi'(y)}}} \right\}$$
$$\times \left\{ \frac{\partial v}{\partial x} dx + \frac{\partial v}{dy} dy \right\} + C_v \left\{ \frac{\partial T}{\partial x} dx + \frac{\partial T}{\partial y} dy \right\} \Bigg] \tag{11}$$

I have also integrated the equation for the case that the difference of the specific heats is a linear function of the temperature, but this seems not necessary in the light of present experimental data.